Thin Solid Films 560 (2014) 49–54

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Donor–π–acceptor organic hybrid $TiO_2$ interfaces for solar energy conversion

Ke Hu [a,b], Kiyoshi C.D. Robson [c,d], Curtis P. Berlinguette [c,d,*], Gerald J. Meyer [a,b,**]

[a] Department of Chemistry, Johns Hopkins University, 3400 North Charles Street, Baltimore, MD 21218, USA
[b] Materials Science & Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, MD 21218, USA
[c] Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary T2N-1N4, Canada
[d] Center for Advanced Solar Materials, University of Calgary, 2500 University Drive N.W., Calgary T2N-1N4, Canada

ARTICLE INFO

Available online 11 September 2013

*Keywords:*
Dye-sensitized
Titanium dioxide
Solar cells
Chenodeoxycholic acid

ABSTRACT

It is reported herein that the co-adsorption of chenodeoxycholic acid (CDCA) with the D–π–A organic dyes (*E*)-3-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (**Dye-O**) or (*E*)-3-(5-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (**Dye-S**) has a significant influence on the ground state absorption spectra of sensitized $TiO_2$ thin films. In the absence of CDCA, evidence for aggregation was observed at even the lowest measured surface coverages. The presence of CDCA also had a significant and very beneficial influence on the unwanted charge recombination reaction between $TiO_2(e^-)$ and oxidized cobalt mediators.

## 1. Introduction

Solar photons are known to initiate a wide variety of technologically and environmentally important reactions at titanium dioxide–organic interfaces [1,2]. At one extreme, the organic molecule is a pollutant that can be degraded to benign chemical products via $TiO_2$ photocatalytic mineralization [3–5]—a popular approach for the clean-up of waste water arising from industry. At another extreme, an organic dye molecule undergoes photo-induced electron transfer reactions that can generate electrical power where no net photochemistry is wanted [6]. Indeed, regenerative dye sensitized solar cells based on anatase $TiO_2$ nanocrystallites cast as a mesoporous thin films have attracted worldwide attention since the seminal report by O'Regan and Gratzel [7]. Remarkable improvements in the efficiency of dye-sensitized solar cells based on organic dye molecules over the last decade, from less than 1% to greater than 9% [8], coupled with their low cost and ease in fabrication, suggest that organic molecules at $TiO_2$ interfaces may one day provide sustainable electrical power for future generations.

A key advance in the efficiency of dye sensitized solar cells with organic dyes was realized by Hara, Arakawa and coworkers in 2004 [9]. With coumarin dye molecules they reported what was at that time an unprecedented 7.5% global conversion efficiency. They also found, as had Gratzel and Kay before them [10], that the presence of deoxycholic acid as a co-adsorbent improved both the photocurrent and the photovoltage of the solar cells. The sensitivity of the energy conversion efficiency of coumarin based dye sensitized solar cells to the presence of deoxycholic acid (and *tert*-butyl pyridine) was remarkable as the global conversion efficiencies without such additives were only 3.6%. To this date, deoxycholic acid, or the related chenodeoxycholic acid (CDCA), shown in Fig. 1 represents common co-adsorbents when organic dyes are utilized in dye sensitized solar cells at metal oxide interfaces. These are naturally occurring bile acids that contain a carboxylic acid functional group, for metal oxide binding, covalently linked through a propylene carbon chain to a steroid-like organic framework. The steroidal portion of the acids contains both hydrophilic and hydrophobic sites that may interact uniquely with different dye molecules; although the details of such putative interactions are not well understood.

A second highly significant advance was made by Licheng Sun and coworkers who replaced coumarin with what are termed 'donor–acceptor,' 'push–pull,' or more specifically 'donor–π–acceptor' type organic dyes [11,12]. The modular nature of these dyes enabled independent optimization of the donor, the π bridge and the acceptor. Furthermore, the orbital arrangement realized when the acceptor was anchored to $TiO_2$, promoted vectorial photo-induced electron transfer towards the $TiO_2$ surface and inhibited thermal back electron transfer to the oxidized donor. Utilization of donor–π–acceptor organic dyes in dye sensitized solar cells resulted in efficiency of 6.7% [13]. Furthermore, it was with this class of dye molecules that high solar conversion efficiencies were first realized with tris–chelated cobalt redox mediators as an alternative to the more standard iodide/tri-iodide mediators [13]. In fact, Wang and coworkers reported an impressive 9.4% conversion efficiency with an organic donor–acceptor sensitizer and $[Co(phen)_3]^{3+/2+}$ redox mediators, where phen is 1,10-phenanthroline [8]. It was later shown that cyclometalated ruthenium polypyridyl dye

---

* Correspondence to: C.P. Berlinguette, Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, T2N-1N4, Canada.
** Correspondence to: G.J. Meyer, Department of Chemistry, Johns Hopkins University, 3400 North Charles Street, Baltimore, MD 21218, USA.
*E-mail addresses:* cberling@ucalgary.ca (C.P. Berlinguette), meyer@jhu.edu (G.J. Meyer).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.08.113

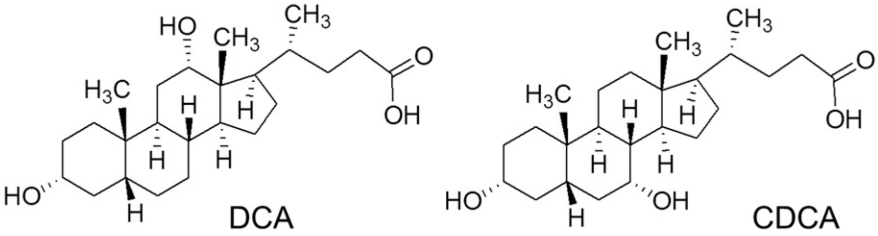

**Fig. 1.** Structure of deoxycholic acid (DCA) and chenodeoxycholic acid (CDCA).

molecules can also be utilized with cobalt redox mediators [14]. Explanations for why cobalt mediators work well under some conditions and not under others remain speculative.

We recently reported the use of two donor–acceptor organic dyes that differed by only a two-heteroatom change from oxygen to sulfur within the donor unit [15]. In solar cells employing either $I_3^-/I^-$ or $[Co(bpy)_3]^{3+/2+}$, where bpy is 2,2′-bipyridine, redox mediators, conversion efficiencies greater than 6% were achieved. Despite similar optical and redox properties for these two donor–π–acceptor organic dyes, a consistently higher open-circuit voltage ($V_{oc}$) was measured with the sulfur containing dye molecule. Mechanistic studies revealed that a 25-fold enhancement of the regeneration rate constant for iodide oxidation enhanced the regeneration yield under open circuit conditions yet had little influence on the yield at the short circuit condition. The data removed the dogma that S atoms were necessarily deleterious for energy conversion with iodide redox mediators [16]. Here we report studies designed to better understand the role of chenodeoxycholic acid and the cobalt mediators on these donor–π–acceptor organic hybrid $TiO_2$ interfaces useful for solar energy conversion.

## 2. Experimental details

### 2.1. Materials

Acetonitrile (Burdick & Jackson, spectrophotometric grade); lithium perchlorate (Aldrich, 99.99%); chenodeoxycholic acid (Alfa Aesar) argon gas (Airgas, >99.998%); oxygen gas (Airgas, industrial grade); titanium(IV) isopropoxide (Sigma-Aldrich, 97%); and glass microscope slides (Fisher Scientific, 1 mm thick). $[Co(bpy)_3](PF_6)_2$ [13] was synthesized according to the literature report. The two dyes were available from previous studies [15].

### 2.2. Substrate preparations

Mesoporous nanocrystalline $TiO_2$ thin films were prepared as previously described. Briefly, $TiO_2$ paste was made by sol–gel method and was doctor-bladed onto glass microscope slides. The slides were then sintered at 450 °C for 30 min under constant $O_2$ flow. The films were kept at 70 °C and then immersed in acetonitrile solution containing dye (~75 μM) and, in some cases, co-adsorbent chenodeoxycholic acid (~3.7 mM). Films were then washed with neat $CH_3CN$ and diagonally positioned in a standard 1 $cm^2$ quartz cuvette in acetonitrile solution for UV–vis spectra measurements. In transient absorption experiments, the sensitized thin films were sandwiched against a glass microscope with a vinyl film (Warps, 8 mil Vinyl-Pane) spacer that contained concentrations of 0.2 M $[Co(bpy)_3]^{2+}$ in 0.5 M $LiClO_4$ acetonitrile solutions. The electrolyte solutions were purged with argon gas for at least 30 min prior to experimentation.

### 2.3. Optical measurements

#### 2.3.1. Steady state UV–vis absorption

Steady state UV–vis absorption spectra were obtained on a Varian Cary 50 spectrophotometer. The macroscopic surface coverage ($\Gamma$ in $mol \cdot cm^{-2}$) was determined from the measured absorption spectra with the modified Beer–Lambert law formula ($Abs = 1000 \times \varepsilon \times \Gamma$), where ε is the molar decadic extinction coefficient in unit of $M^{-1} \cdot cm^{-1}$. The peak molar decadic extinction coefficient of the sensitized $TiO_2$ film was assumed to have the same value as in solution. All experiments were performed at room temperature.

#### 2.3.2. Transient absorption spectroscopy

Nanosecond transient absorption measurements were obtained with an apparatus similar to that which has been previously described [17]. Briefly, samples were excited with nanosecond pulses of 532 nm light with a 150 W Xenon lamp as the probe beam. Optical filters were used to remove IR, UV and scattered light. Kinetic analysis was performed in Origin 8.

## 3. Results and discussion

The molecular structures of the dye molecules are (*E*)-3-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (**Dye-O**) and (*E*)-3-(5-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (**Dye-S**) shown in Fig. 2. These molecules were prepared and characterized in a previously reported manuscript [15].

### 3.1. Surface coverage effect of **Dye-O** and **Dye-S** on UV–vis absorption spectra

Surface coverages of **Dye-O**/$TiO_2$ and **Dye-S**/$TiO_2$ were varied by immersing $TiO_2$ films in 75 μM $CH_3CN$ solutions with 3.7 mM CDCA for different periods of time. With this approach, about a factor of ten change in surface coverage was realized based on UV–vis absorption spectroscopy, Figs. 3a and 4a. The absorption maximum progressively shifted towards the blue, i.e., a hypsochromic shift. This is most easily seen in the normalized spectra shown in Figs. 3b and 4b. Indeed the surface coverage was directly correlated with the absorption maximum. Note that the oscillation in the “absorption spectra”, that are most pronounced at low surface coverages, are interference patterns from the thin films.

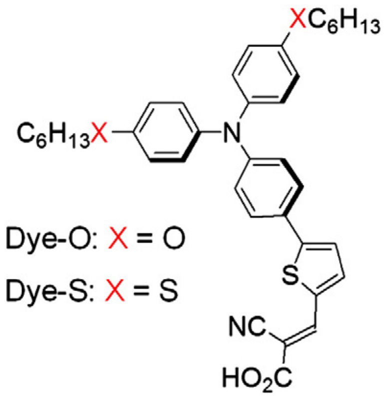

**Fig. 2.** Molecular structure of the two organic dyes **Dye-O** and **Dye-S**.

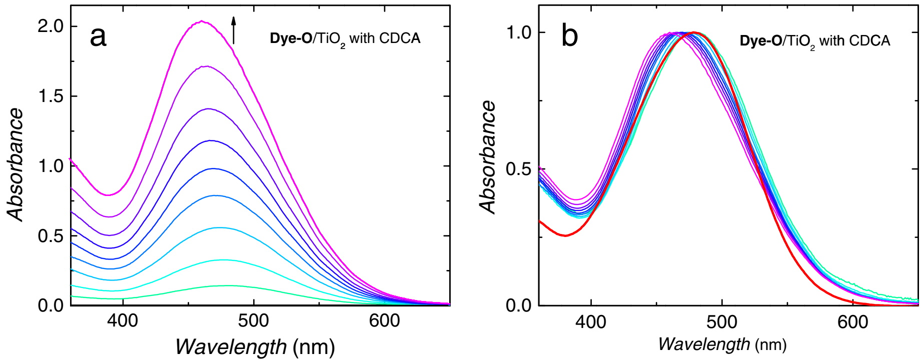

**Fig. 3.** (a) Ground state absorption spectra of **Dye-O**/$TiO_2$ immersed in neat $CH_3CN$ at different surface coverages ($5.1 \times 10^{-9}$–$7.2 \times 10^{-8}$ mol·cm$^{-2}$). (b) Normalized absorption spectra for all surface coverages of **Dye-O**/$TiO_2$. Overlaid in thick red is the **Dye-O** solution spectrum in neat $CH_3CN$. The arrow shows the direction for increasing surface coverages.

Comparisons of the **Dye-O** or **Dye-S** solution spectra with that measured for the sensitized thin film were made. The absorption maximum of **Dye-O** was 478 nm ($\varepsilon = 2.84 \times 10^4$ M$^{-1}$·cm$^{-1}$) and for **Dye-S** was 469 nm ($\varepsilon = 3.16 \times 10^4$ M$^{-1}$·cm$^{-1}$) in fluid $CH_3CN$ solution. The absorption maxima measured for the sensitized films were most similar to these values when the dye surface coverage was the lowest. At higher surface coverages, the absorption maximum of **Dye-O**/$TiO_2$ was blue shifted 730 cm$^{-1}$ and **Dye-S**/$TiO_2$ by 900 cm$^{-1}$ relative to these solution values, behavior attributed to dye aggregation as is discussed in the next section. In addition, the long wavelength absorption onset for the highest surface coverage films was red shifted by about 1010 cm$^{-1}$ (from 610 nm to 650 nm) for **Dye-O** and 540 cm$^{-1}$ (from 600 nm to 620 nm) for **Dye-S**. This change in the absorption onset has previously been observed for ruthenium polypyridyl and coumarin dyes and was attributed to increased delocalization of the carboxylate group into the organic π system upon binding with $Ti^{4+}$ site on the surface [18,19]. While such an interpretation seems reasonable, it is difficult to rule out intermolecular interaction between the dye molecules that could also influence the absorption onset.

### 3.2. Effect of CDCA coadsorption on UV–vis absorption spectra

Aggregation of some dye molecules is known to quench photoluminescence and hence is often expected to decrease the excited state injection yield and hence the overall solar cell efficiency [20,21]. As mentioned in the Introduction section, chenodeoxycholic acid (CDCA) has been used extensively at organic $TiO_2$ interfaces with the notion that it inhibits dye aggregation on the $TiO_2$ surface [9,19]. Most commonly as was done in this study, this additive is placed in the dying solution such that the CDCA molecules competitively co-adsorb with the dye molecules. This co-adsorption procedure has been particularly effective when coumarin dye molecules were employed, even though it decreased the total number of dyes present at the interface [9]. Computational chemistry has shown that CDCA molecules insert themselves between coumarin molecules thereby inhibiting intermolecular dye–dye interaction [22]. To test whether similar behavior might occur for these donor–π–acceptor dye molecules, surface adsorption studies were performed in the absence of CDCA. By varying the amount of time the $TiO_2$ was allowed to react with the organic dye molecules, the surface coverage could again be varied by over a factor of ten. However, the spectra were quantitatively different from these measured with CDCA. The hypsochromic shift in the absorption spectrum was evident in even the lowest surface coverage data, Figs. 5 and 6. Indeed the normalized spectra show that the absorption maximum were almost surface coverage independent which is in stark contrast to that observed when CDCA was present and a progressive blue shift was observed with increased surface coverage. The dramatic changes in the absorption maximum with surface coverage, that were significantly smaller in the presence of CDCA, are most easily observed in the plot shown in Fig. 7. This data supports the theoretical predictions and suggests that these donor–π–acceptor dye molecules are aggregated, even at the lowest surface coverages [22].

### 3.3. Surface coverage effect on charge recombination between $TiO_2(e^-)$ and $[Co(bpy)_3]^{3+}$

Due to the intrinsic two electron redox chemistry of $I_3^-$, charge recombination between $TiO_2(e^-)$ in isolated states and $I_3^-$ is thought to be rare in operational solar cells [23]. The disadvantage of utilizing

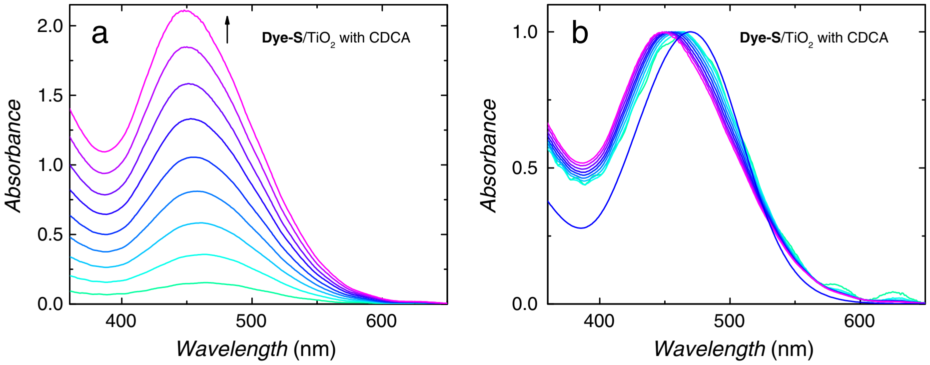

**Fig. 4.** (a) Ground state absorption spectra of **Dye-S**/$TiO_2$ immersed in neat $CH_3CN$ at different surface coverages ($4.9 \times 10^{-9}$–$6.7 \times 10^{-8}$ mol·cm$^{-2}$). (b) Normalized absorption spectra for all surface coverages of **Dye-S**/$TiO_2$. Overlaid in thick blue is the **Dye-S** solution spectrum in neat $CH_3CN$. The arrow shows the direction for increasing surface coverages.

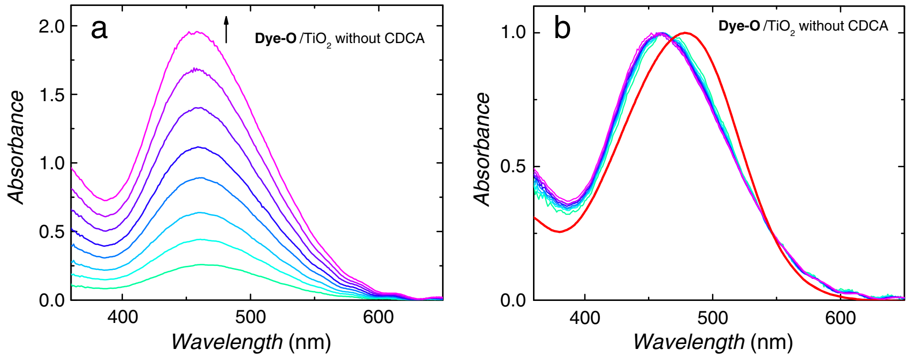

**Fig. 5.** (a) Ground state absorption spectra of **Dye-O**/$TiO_2$ in neat $CH_3CN$ without chenodeoxycholic acid at different surface coverages ($8.8 \times 10^{-9}$–$6.9 \times 10^{-8}$ mol·cm$^{-2}$) and (b) their normalized spectra. Overlaid in thick red is the **Dye-O** solution spectrum in neat $CH_3CN$. The arrow shows the direction for increasing surface coverages.

$I_3^-/I^-$ redox mediator is that the one electron oxidation of $I^-$ induces a series of I–I bond formation and disproportionation reactions that are accompanied by a free energy loss of around 600 mV [24]. This has motivated extensive explorations of alternative redox mediators and cobalt based coordination compounds appear to be the most promising. Indeed, an efficiency of over 12% was achieved by Gratzel's group utilizing a zinc porphyrin with long alkyl chains and $Co^{III/II}$tris(bipyridyl) compounds as the redox mediator [25]. The long chain hydrocarbon was introduced to block close approach of the cobalt mediators with the $TiO_2$ surface. It was of interest to see whether evidence for such behavior could be observed by simply increasing the number of **Dye-O** or **Dye-S** molecules on the $TiO_2$ surface.

To accomplish this, nanosecond transient absorption spectroscopy was employed. Pulsed laser excitation of a **Dye-S**/$TiO_2$ thin film in a 0.5 M $LiClO_4/CH_3CN$ solution that contained 0.2 M $[Co(bpy)_3]^{2+}$ led to the immediate appearance of the oxidized sensitizer and an injected electron, Eq. (1). Consistent with previous studies the rate constant for excited state injection could not be time resolved with nanosecond resolution, $k_{inj} > 10^8\ s^{-1}$.

$$\mathbf{Dye}-\mathbf{S}^*/TiO_2 \rightarrow \mathbf{Dye}-\mathbf{S}^+/TiO_2(e^-). \tag{1}$$

The oxidized dye was then regenerated by the $[Co(bpy)_3]^{2+}$ present in the solution, Eq. (2).

$$Dye-\mathbf{S}^+/TiO_2(e^-) + Co^{II}(bpy)_3^{2+} \rightarrow Dye-\mathbf{S}/TiO_2 + Co^{III}(bpy)_3^{2+}. \tag{2}$$

This dye regeneration reaction was previously characterized under pseudo-first order conditions and the rate constants were found to be $1.1 \times 10^6\ M^{-1}\ s^{-1}$ for **Dye-O**$^+$/$TiO_2$ and $3.5 \times 10^6\ M^{-1}\ s^{-1}$ for **Dye-S**$^+$/$TiO_2$. The approximately 3-fold larger rate constant for **Dye-S**$^+$/$TiO_2$ presumably stems from the 70 mV more favorable driving force for the reaction, $\Delta G° = -0.53$ V versus $-0.46$ V [15].

The subsequent reaction of the injected electron with the oxidized cobalt compound has not been previously reported. This recombination reaction was studied for **Dye-S**/$TiO_2$ at low $7.0 \times 10^{-9}$ mol cm$^{-2}$ and high $3.5 \times 10^{-8}$ mol cm$^{-2}$ surface coverages without the presence of CDCA, Eq. (3).

$$Dye-\mathbf{S}/TiO_2(e^-) + Co^{III}(bpy)_3^{2+} \rightarrow Dye-\mathbf{S}/TiO_2 + Co^{II}(bpy)_3^{2+}. \tag{3}$$

This reaction was difficult to monitor as the $TiO_2(e^-)$ and the cobalt compounds absorb light only very weakly in the visible region. Furthermore, the oxidized organic dyes absorb throughout the visible region that makes selective monitoring of reaction (3) impossible. An observation wavelength of 740 nm was selected where the $TiO_2(e^-)$s have an extinction coefficient of approximately 1000 $M^{-1}\ cm^{-1}$. While the oxidized triphenylamine groups absorb light more strongly at this wavelength, the regeneration reaction were sufficiently separated in time that recombination reaction (3) could be cleanly observed.

Shown in Fig. 8 are representative kinetics monitored at 740 nm after pulsed 532-nm excitation of **Dye-S**/$TiO_2$. The first ten microseconds corresponded to the regeneration reaction, Eq. (2). On longer time scales,

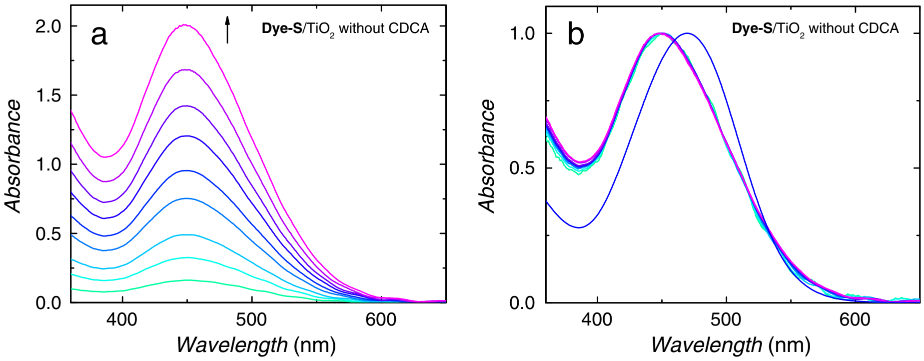

**Fig. 6.** (a) Ground state absorption spectra of **Dye-S**/$TiO_2$ in neat $CH_3CN$ without chenodeoxycholic acid at different surface coverages ($5.1 \times 10^{-9}$–$6.4 \times 10^{-8}$ mol·cm$^{-2}$) and (b) their normalized spectra. Overlaid in thick blue is the **Dye-S** solution spectrum in neat $CH_3CN$. The arrow shows the direction for increasing surface coverages.

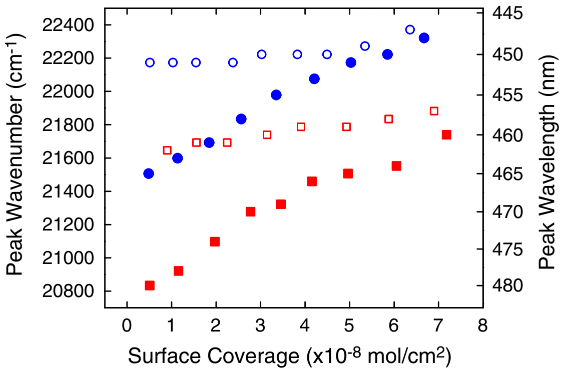

**Fig. 7.** Plot of the absorption maximum in wavenumbers and wavelength for **Dye-O**/$TiO_2$ (solid red squares: with CDCA coadsorption; open red squares: without CDCA coadsorption) and **Dye-S**/$TiO_2$ (solid blue circles: with CDCA coadsorption; open blue circles: without CDCA coadsorption) versus the surface coverages.

the positive absorption was due to $TiO_2(e^-)$s and provided a means for the study of charge recombination reaction (3). The kinetics were non-exponential and could be well described by a stretched exponential equation, i.e., Kohlrausch–Williams–Watts (KWW) model, Eq. (4) [26,27]. Average rate constants were calculated at the first moment by Eq. (5), the values of which are summarized in Table 1.

$$\Delta Abs = A\exp\left[-(kt)^{\beta}\right] \tag{4}$$

$$k_{cr} = \left[(1/k\beta)\times\Gamma(1/\beta)\right]^{-1}. \tag{5}$$

The raw experimental data shows that only minimal differences were observed for the low and high surface coverage thin films. Analysis by the KWW function revealed average rate constants of 310 $s^{-1}$ that are over a hundred times faster than the corresponding reactions with $I_3^-$, 2.3 ± 0.4 $s^{-1}$ [15]. It is puzzling that the recombination rate constants were surface coverage independent within experimental error. Contrary to what was observed, one might have anticipated that at lower surface coverages larger areas of the unsensitized $TiO_2$ surface would be exposed to the solution where $[Co(bpy)_3]^{3+}$ would have a close approach resulting in faster recombination. Although speculative, it may be that under these conditions, there exists a sufficient area of exposed $TiO_2$ to enable close approach by the oxidized cobalt acceptors. If this were the case, the data would be consistent with the conclusion drawn from the steady state absorption spectra: in the absence of CDCA the dye molecules are aggregated and the average distance between them does not appear to change with the total number of dye molecules present on the surface. This conclusion is also in agreement with a similar data reported for inorganic dye molecules [28].

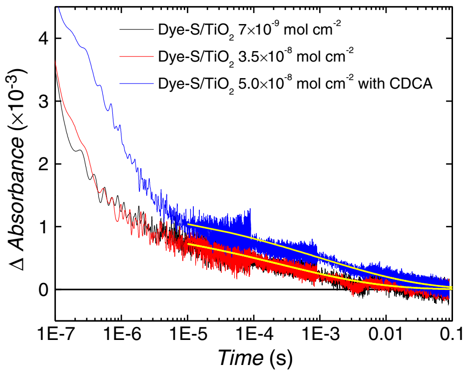

**Fig. 8.** Absorption changes monitored at 740 nm after pulsed 532 nm light excitation of **Dye-S**/$TiO_2$ in 0.5 M $LiClO_4$ and 0.2 M $[Co(bpy)_3]^{2+}$ $CH_3CN$ solution. Data were recorded for surface coverages of $7\times10^{-9}$ mol $cm^{-2}$ (black) and $3.5\times10^{-8}$ mol $cm^{-2}$ (red). Data is also shown for a $5.0\times10^{-8}$ mol $cm^{-2}$ **Dye-S**/$TiO_2$ with chenodeoxycholic acid as coadsorbent (blue). Overlaid in yellow are fits to the KWW function as is described in the text.

**Table 1**
Charge recombination rate constants abstracted from KWW modeling at different surface coverages of **Dye-S**/$TiO_2$.

| Surface coverage of **Dye-S**/$TiO_2$ ($mol\cdot cm^{-2}$) | $k$ ($s^{-1}$) | β | $k_{cr}$ ($s^{-1}$) |
|---|---|---|---|
| $7.0\times10^{-9}$ | $4.0\times10^{3}$ | 0.28 | $3.1\times10^{2}$ |
| $3.5\times10^{-8}$ | $4.0\times10^{3}$ | 0.28 | $3.1\times10^{2}$ |
| $5.0\times10^{-8}$ with CDCA | $1.0\times10^{3}$ | 0.28 | $7.8\times10^{1}$ |

The influence of CDCA on charge recombination to the oxidized cobalt mediators was also investigated. Surprisingly, the regeneration step appeared to be slower to the presence of the CDCA co-adsorbent with **Dye-S**, Fig. 8. This observation is important and the generality of it with other organic dye molecules and under other experimental conditions will be the subject of a future publication. On 10 μs and longer time scales, reaction of the injected electron and the oxidized cobalt mediator could be clearly observed. The kinetics were again non-exponential and analysis by the KWW model showed that the average charge recombination rate constant was 4-fold smaller. Indeed the average rate constant was much more comparable to that reported for recombination to $I_3^-$. This could indeed be attributed to a more uniform blocking layer induced by the CDCA co-adsorbent.

## 4. Summary

We have shown that the co-adsorption of CDCA and D–π–A organic dyes has a significant influence on the ground state absorption spectra of sensitized $TiO_2$ thin films. In the absence of CDCA, evidence for aggregation was observed at even the lowest surface coverages. The presence of CDCA also had a significant influence on the unwanted charge recombination reaction between $TiO_2(e^-)$ and oxidized cobalt mediators.

## Acknowledgments

G.J.M and K.H. work was funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-FG02-96ER14662. CPB and KCDR are grateful to the Canadian Natural Science and Engineering Research Council, Canadian Foundation for Innovation, Alberta Innovates and the Canada School of Energy and Environment (CSEE) for support.

## References

[1] H. Gerischer, F. Willig, Top. Current Chem., vol. 61, Springer, Berlin Heidelberg, 1976. 31.
[2] H.O. Finklea, Semiconductor Electrodes, Elsevier, Amsterdam, Netherlands, 1988.
[3] K. Rajeshwar, M.E. Osugi, W. Chanmanee, C.R. Chenthamarakshan, M.V.B. Zanoni, P. Kajitvichyanukul, R. Krishnan-Ayer, J. Photochem. Photobiol. C: Photochem. Rev. 9 (4) (2008) 171.
[4] A. Mills, M. Sheik, C. O'Rourke, M. McFarlane, Appl. Catal. B Environ. 89 (1–2) (2009) 189.
[5] A.J. Julson, D.F. Ollis, Appl. Catal. B Environ. 65 (3–4) (2006) 315.
[6] A. Mishra, M.K.R. Fischer, P. Bäuerle, Angew. Chem. Int. Ed. 48 (14) (2009) 2474.
[7] B. O'Regan, M. Grätzel, Nature 353 (6346) (1991) 737.
[8] Y. Bai, J. Zhang, D. Zhou, Y. Wang, M. Zhang, P. Wang, J. Am. Chem. Soc. 133 (30) (2011) 11442.
[9] K. Hara, Y. Dan-oh, C. Kasada, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, Langmuir 20 (10) (2004) 4205.
[10] A. Kay, M. Graetzel, J. Phys. Chem. 97 (23) (1993) 6272.
[11] D.P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, Chem. Commun. (21) (2006) 2245.
[12] D.P. Hagberg, J.-H. Yum, H. Lee, F. De Angelis, T. Marinado, K.M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel, M.K. Nazeeruddin, J. Am. Chem. Soc. 130 (19) (2008) 6259.

[13] S.M. Feldt, E.A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, J. Am. Chem. Soc. 132 (46) (2010) 16714.
[14] P.G. Bomben, T.J. Gordon, E. Schott, C.P. Berlinguette, Angew. Chem. Int. Ed. 50 (45) (2011) 10682.
[15] K.C.D. Robson, K. Hu, G.J. Meyer, C.P. Berlinguette, J. Am. Chem. Soc. 135 (5) (2013) 1961.
[16] B.C. O'Regan, K. Walley, M. Juozapavicius, A. Anderson, F. Matar, T. Ghaddar, S.M. Zakeeruddin, C.D. Klein, J.R. Durrant, J. Am. Chem. Soc. 131 (10) (2009) 3541.
[17] R. Argazzi, C.A. Bignozzi, T.A. Heimer, F.N. Castellano, G.J. Meyer, Inorg. Chem. 33 (25) (1994) 5741.
[18] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Graetzel, J. Am. Chem. Soc. 115 (14) (1993) 6382.
[19] Z.-S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, J. Phys. Chem. B 109 (9) (2005) 3907.
[20] P.K. Ghosh, A.J. Bard, J. Phys. Chem. 88 (23) (1984) 5519.
[21] J. He, G. Benkö, F. Korodi, T. Polívka, R. Lomoth, B. Åkermark, L. Sun, A. Hagfeldt, V. Sundström, J. Am. Chem. Soc. 124 (17) (2002) 4922.
[22] M. Pastore, F. De Angelis, J. Phys. Chem. Lett. 4 (6) (2013) 956.
[23] J.G. Rowley, B.H. Farnum, S. Ardo, G.J. Meyer, J. Phys. Chem. Lett. 1 (20) (2010) 3132.
[24] G. Boschloo, A. Hagfeldt, Acc. Chem. Res. 42 (11) (2009) 1819.
[25] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, Science 334 (6056) (2011) 629.
[26] G. Williams, D.C. Watts, Trans. Faraday Soc. 66 (0) (1970) 80.
[27] C.P. Lindsey, G.D. Patterson, J. Chem. Phys. 73 (7) (1980) 3348.
[28] B. O'Regan, L. Xiaoe, T. Ghaddar, Energy Environ. Sci. 5 (5) (2012) 7203.